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Recombination pathways in polymer:fullerene photovoltaics observed through spin polarization measurements

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We report magnetoconductance measurements on polymer:fullerene photovoltaic devices in the regime of high fields and low temperatures, where spin polarization of injected carriers plays an important role. The current either decreases or increases with magnetic field, depending on whether the interfacial charge-transfer state lies above or below the intramolecular triplet state in energy. Rapid transitions from triplet charge-transfer states to lower-lying triplet excitons constitute an important loss mechanism that is responsible for the negative magnetoconductance observed. © *2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4865203]

Organic photovoltaics (OPVs) offer the potential for cheap large-area processing but are held back by efficiencies which remain lower than conventional inorganic photovoltaics despite rapid recent improvements.[1–4] Key challenges to reach the highest level of efficiency include eliminating geminate recombination of charge pairs formed by charge transfer (CT) at the donor-acceptor heterojunction,[5–9] reducing the energy required to drive the charge transfer reaction,[10,11] and reducing the rate constant for unnecessary bimolecular recombination so that the operating voltage approaches the maximum possible value for the materials involved.[12,13] Recently, increasing attention has focused on the role of spin in controlling recombination in OPVs.[14] As shown in Figure 1(a), the charge-transfer state formed by dissociation of a photogenerated singlet exciton will have singlet character (^{1}CT) and is liable to recombine to the singlet ground state if it is not rapidly dissociated into free charges. Intersystem crossing from ^{1}CT to the triplet (^{3}CT) charge-transfer state may occur, and this state is less likely to recombine to the ground state before dissociation. However, where there is an energetically lower-lying intramolecular triplet exciton state (T_1), this state may be rapidly formed from the ^{3}CT state. These tightly-bound T_1 states are typically hard to dissociate, so their formation is a terminal loss mechanism. Similar effects arise in bimolecular recombination, where ^{1}CT and ^{3}CT states are formed in a 1:3 ratio, as in an organic light-emitting diode (LED). If the ^{3}CT state is long-lived, it may redissociate into charges, thus reducing the net bimolecular recombination rate. One way to avoid formation of T_1 from ^{3}CT states is to arrange for the CT states to be lower in energy than T_1. However, this requires a large amount of energy to be dissipated in the S_1 to ^{1}CT transition and is therefore incompatible with a high open-circuit voltage. Recently, it has been shown that even when T_1 is the lowest-energy state, in some systems the transition from ^{3}CT to T_1 is sufficiently slow that ^{3}CT states are efficiently dissociated.[14]

Magnetic fields provide a useful way to control spin populations in devices, and a wide range of resulting magnetic field effects (MFEs) have been reported in organic devices.[15–22] We have recently reported that at very high fields and low temperatures, carriers injected into organic LEDs and photovoltaics can become spin polarized, meaning that bimolecular recombination leads only to the formation of triplet states.[23] In P3HT:PCBM devices, a photovoltaic system where the CT states lie below the T_1 state, spin polarization leads to the preferential formation of long-lived ^{3}CT states that can be redissociated, thus suppressing the net rate of bimolecular recombination and increasing the dark current by up to 50%. These results are rather unexpected, hence more work to substantiate the underlying model is desirable. Furthermore, the ability to directly control the spin of CT states allows a sensitive test of models for spin-dependent recombination in different photovoltaic systems.

In the current work, we extend these measurements to a range of polymer:fullerene devices, where the energy separation and ordering of the ^{3}CT and T_1 states can be varied. In systems where T_1 is the lowest state, the MFE becomes negative rather than positive, clearly identifying bimolecular recombination to T_1 as a terminal loss mechanism in these systems. Energies of CT states are determined by monitoring the weak luminescence from ^{1}CT, and the magnetic field dependence of this emission provides further confirmation for the spin polarization model.

The chemical structures of the materials used are shown in Figure 1(b). The active layers in the photovoltaic device structures were poly(3-hexylthiophene) (P3HT) blended with [6,6]-phenyl C_{61} butyric acid methyl ester ($PC_{60}BM$), and poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV), poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT), poly[N-9′-heptadecanyl-2,7-carbazole-alt-5, 5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) and poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′] dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl] thieno[3,4-b]thiophenediyl}) (PTB7) each blended with [6,6]-phenyl C_{71} butyric acid methyl ester ($PC_{70}BM$). Devices were fabricated with the structure glass/indium tin oxide

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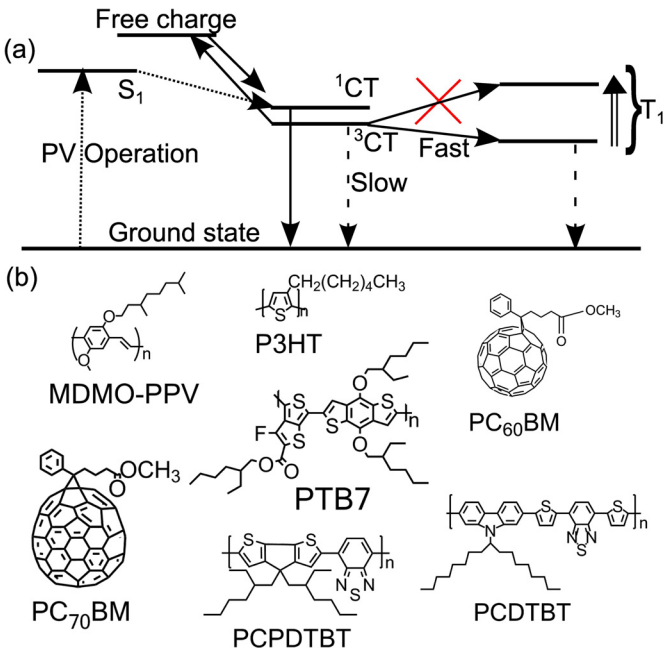

FIG. 1. (a) Excited state energies and kinetic processes in a donor-acceptor photovoltaic blend. (b) Chemical structures of the materials used.

(ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/active layer/aluminum. Hole-only devices were also made using the same structure but with palladium in place of aluminum. The active layer was spin-coated from solution to produce films of approximately 100 nm thickness. The devices were placed in the sample space of a Cryogenic Ltd 10 T split-pair optical cryo-magnetic system with integral variable temperature insert to perform dark current measurements in a temperature-controlled helium atmosphere. Electroluminescence, which is attributed to ^{1}CT emission, was measured using a fiber-coupled spectrograph with an InGaAs CCD camera, either at room temperature in an integrating sphere, or *in-situ* in the magnet.

Figure 2 shows the effect of magnetic field on the dark current in each device at 2 K and at fixed biases chosen to give currents of 0.08 mA/cm^2 at zero magnetic field. P3HT:$PC_{60}BM$ shows a large positive effect as reported previously,[23] whereas MDMO-PPV:$PC_{70}BM$ shows a smaller positive effect and the other blends show negative

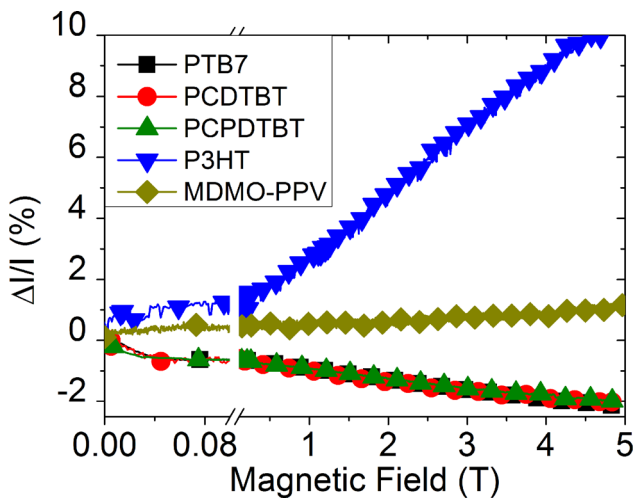

FIG. 2. Magnetoconductance in the dark current of polymer:fullerene photovoltaic devices at 2 K, measured at constant biases chosen to give a current density of 0.08 mA/cm^2 at zero field.

effects. The effects seen are much stronger than any effects seen in hole-only devices (see supplementary material[24]) and are therefore associated with changes in electron-hole recombination. We focus here on the high-field effects, which only appear at low temperatures (see supplementary material[24]), consistent with a spin polarization effect. As explained above, in materials showing a positive effect, preferential recombination to the long-lived ^{3}CT state allows more time for redissociation of the CT state, reducing the net rate of bimolecular recombination. Reduced recombination leads to increased current, since the region of overlap of electron and hole densities becomes more extended, thus reducing space-charge limitations on the current. For devices where both electron and hole currents are space-charge-limited, these effects can be modeled quantitatively according to the theory of Parmenter and Ruppel.[25] For the devices where a negative MFE is seen, we propose that this is due to the T_1 state being below ^{3}CT, leading to rapid losses of ^{3}CT states to T_1 before redissociation can occur. Increasing the formation of ^{3}CT states through spin polarization thus leads to increased net recombination and reduced current.

TABLE I Energies of the singlet exciton (S_1), charge-transfer state (CT), and triplet exciton (T_1) in the polymers used.

Material	S_1 (eV)	^{3}CT (eV)	T_1 (eV)
P3HT	2.05[a]	1.3	1.40[b]
MDMO-PPV	2.1[c]	1.35	1.40[b]
PCPDTBT	1.76[d]	1.2	1.0[e]
PCDTBT	1.86[f]	1.35	1.16
PTB7	1.6[g]	1.27	0.9

[a]Reference 31.
[b]Reference 10.
[c]Reference 32.
[d]Reference 33.
[e]Reference 34.
[f]Reference 35.
[g]Reference 2.

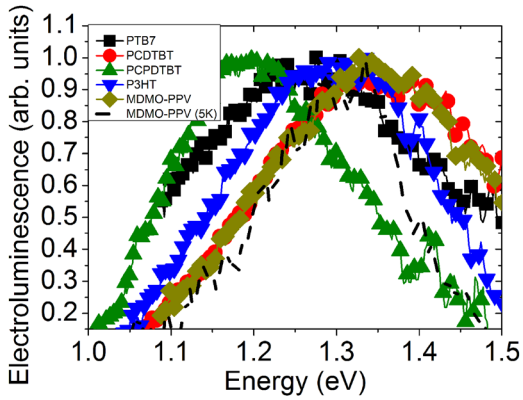

FIG. 3. Electroluminescence spectra of polymer:fullerene blend devices at room temperature (symbols) and low temperature (dashed line) under positive bias.

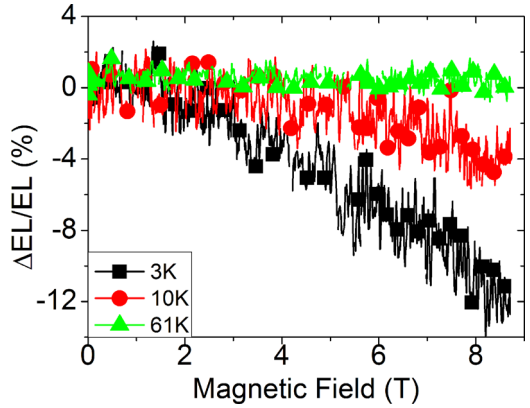

FIG. 4. Fractional change in electroluminescence intensity with magnetic field for an MDMO-PPV:$PC_{70}BM$ blend device measured at constant voltages of 4.3 V, 4.3 V, and 3.7 V to give a current density of 0.08 mA/cm^2 at zero field for temperatures of 3 K, 10 K, and 61 K, respectively.

To confirm this proposal, we compare our data with independent measurements of the CT and triplet state energies, as shown in Table I. The ^{3}CT and ^{1}CT states are very close in energy, even at high fields,[26] so we can determine the ^{3}CT energy from the peaks of the electroluminescence spectra (Figure 3) which are attributed to emission from ^{1}CT states formed by bimolecular recombination. The energies of T_1 states are more difficult to determine. In some of our materials, measurements of these energies by triplet sensitization experiments have been reported,[10] and for others we use the empirical rule due to Köhler that the triplet state lies 0.7 eV below the absorption onset,[27] an approach that has proved successful in detailed spectroscopic studies of CT and T_1 states in photovoltaic blends.[28,29] From Table I, there is a clear connection between the sign of the observed MFE and the relative ordering of the CT and T_1 states.

We note that we also observe distinct changes in dark current at low fields (<100 mT). These effects have been widely studied[16–19] and are attributed to a reduction in intersystem crossing once the external field exceeds the hyperfine field.[20–22] We note that in the low-field regime intersystem crossing takes place in charge pairs sufficiently separated to have negligible exchange energy;[30] these charge pairs coexist with more tightly bound CT states that have sufficient wavefunction overlap to recombine to the ground state or to T_1. We find that in each case, the sign of the low-field effect matches that seen at high fields. Negative low-magnetic-field effects are expected when the zero-field intersystem crossing rate is larger than the other rates, the dissociation rate for CT states is comparable with the rate of formation of T_1 from ^{3}CT, and the recombination rate from ^{1}CT is lower than the other rates.[24] The effect becomes positive as the rate of T_1 formation is reduced, consistent with the observed change as T_1 moves above ^{3}CT in energy.

As further confirmation of the role of spin-dependent bimolecular recombination when spins are polarized, we have investigated the magnetic field dependence of the electroluminescence in MDMO-PPV:$PC_{70}BM$ devices (Figure 4). At low temperatures, there is a substantial decrease in electroluminescence with field (despite the slight increase in current). This is consistent with preferential formation of non-emissive ^{3}CT states as predicted. Whilst some of these states might be redissociated and have another chance to recombine, the rest will decay non-radiatively to the ground state (consistent with the small positive effect seen in the current for this system). Thus, the fraction of recombination that is radiative is reduced by spin polarization, as seen previously in conventional LED systems.[23]

Our measurements clearly demonstrate a change in sign of the magnetic field effect on the dark current in photovoltaic blend devices depending on the energetic ordering of the charge-transfer and triplet exciton states. Combined with measurement of emission from charge-transfer states, these results establish a detailed picture of spin-dependent recombination pathways in photovoltaic systems, identifying recombination pathways through triplet states that can be an important loss mechanism in devices. These measurements establish a useful method to determine the energetic position of triplet states whose energies are difficult to measure directly.

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